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ABSTRACT

Extraction and stripping kinetics of lactic acid in extractive fermentation were studied using tri-*n*-octylmethylammonium chloride, a quaternary ammonium salt, as an extractant and oleyl alcohol as a diluent. The kinetic analysis was performed through simulated time course studies of lactate concentration in both the extraction and stripping phases. Dependences of extraction rate on initial lactate and extractant concentrations and those of stripping rate on initial chloride and extractant-lactate complex concentrations were examined. Because diffusion through the organic film was a rate-controlling step, the experimental results of both extraction and stripping could be explained well by a simple equation.

Key Words: Lactic acid; Quaternary ammonium salt; Extraction kinetics; Mass transfer coefficient

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INTRODUCTION

The demand of L-lactic acid as the raw material of a biodegradable polymer is increasing (1–2). When lactic acid is synthesized by a chemical method, the L-isomer is difficult to separate out of the racemic mixture obtained. Because a fermentation method can directly produce the L-isomer with high optical purity, it has received increased attention. However, the recovery and purification of lactic acid from fermented broth is difficult, and separation costs are a high percentage of the total cost. The solvent extraction method has advantages; for example, pretreatment is unnecessary and large amounts can be processed easily (3–8). The simultaneous operation of fermentation and extraction has further merits because it prevents product inhibition and can be used to realize more effective production.

We investigated the extractive fermentation process to produce L-lactic acid efficiently (9–11). The extractant suitable for extractive fermentation was selected based on its extractability potential and toxicity to microbes. Though both di-*n*-octylamine (DOA) and tri-*n*-octylmethylammonium chloride (TOMAC) showed high extraction rates around the pH optimum for fermentation, the DOA-lactate complex deposited in the organic phase was unstable. In addition, TOMAC was strongly toxic to microbes because it is a quaternary ammonium salt with ion exchange ability. However, we found that TOMAC dissolved in water could be removed easily by a cleaning column packed with cation-exchange resin (11). Therefore, TOMAC was selected as an optimum extractant for the extractive fermentation and was diluted with oleyl alcohol that had no toxicity. The extractive fermentation was possible with TOMAC/oleyl alcohol as the extraction solvent, but the productivity was not improved over conventional fermentation as had been expected; the lactic acid produced could not be recovered satisfactorily. To find a way to accelerate the recovery, extraction kinetics of lactic acid were studied in detail.

The extraction equilibria of carboxylic and citric acids that were extracted with phosphoric and amine extractants has been reported by many researchers (12–18). However, only a few researchers have reported studies on the extraction kinetics of these systems. The kinetics of carboxylic acid extraction with phosphoric extractant and amino acid extraction with quaternary ammonium salt were reported by Matsumoto et al. and Uddin et al. (19–21). They explained the observed extraction rates based on the 2-film theory because the anion exchange reaction by TOMAC was very rapid and the diffusion processes were the rate-controlling steps. The kinetics of citric acid extraction with amine was reported by Jaung and Haung (22). They concluded that the extraction rate was mainly controlled by a chemical reaction occurring at the organic side of the liquid-liquid interface. We found no report on the rate of lactic acid extraction with TOMAC.

In this study, the kinetics of extraction and stripping in lactic acid recovery were examined to clarify the effect of operating conditions. By applying the 2-film theory to the TOMAC/oleyl alcohol system, we describe the kinetics of lactic acid extraction.

EXPERIMENTAL

Chemicals

L-lactic acid was purchased from the Wako Pure Chemical Industry Co, Ltd, (Tokyo, Japan) and lactate was prepared by refluxing for more than 10 hours for monomerization and the pH was adjusted to 6.0 with a 25% aqueous ammonium solution. TOMAC of industrial grade (purity = 81.0%), kindly supplied by Koei Chemical Industry Co, Ltd, was used without further purification. Oleyl alcohol was purchased from Kishida Chemistry Co, Ltd. The crystalline lactic acid, used as a standard for analysis, was of analytical grade (purity $> 99.2\%$) and was from Kanto Chemical Co, Ltd. Except for TOMAC, the chemicals used were of analytical grade.

Extraction of Lactate

The extraction of lactate was performed through the use of a Lewis-type stirred cell with constant interfacial area. Aqueous and organic solutions of the same volume were stirred independently at 40 rpm by two 6-blade paddles rotating in opposite directions. The volume of each phase was 0.150×10^{-3} m^3, and the interfacial area was 4.43×10^{-3} m^2. The feed solution was initially introduced into a transfer cell. The prepared organic solution was then poured carefully into the cell so the interface was not disturbed. The temperature of the cell was kept at 25°C by the water from an external thermostatic bath that circulated through an insulating jacket. Aqueous ammonium lactate solutions of 0.1–0.9 kmol/m^3 were used as the aqueous phase. These aqueous solutions were prepared by diluting the lactate solution with pure water (no buffer). Oleyl alcohol solutions of 0.1–0.5 kmol/m^3 TOMAC were used as the organic phase. Each kinetic run was continued for approximately 6 hours, and samples were withdrawn from both phases simultaneously at regular time intervals during each run. After each kinetic run, to obtain the equilibrium constant, the aqueous and organic phases were completely mixed for 30 minutes at stirring rates increased up to 120 minutes.

Stripping of Lactate

The stripping runs were performed with the operation similar to that used for extractions. Aqueous sodium chloride solutions of 0.03–3.0 kmol/m^3

(0.175–17.5% (wt)) were used as stripping solutions. Tri-*n*-octylmethylammonium (TOMA) cation and lactate anion complexes of 0.05–0.15 kmol/m^3 (0.445–1.34% (wt) lactate) were used as the organic phase. These complexes were prepared by extracting lactate of appropriate concentration with 0.5 kmol/m^3 TOMAC/oleyl alcohol.

Chemical Analysis

The concentration of lactate in the aqueous phase was measured by a high-performance liquid chromatography (HPLC) system that consisted of a Shimazu LC-6A HPLC pump and Shimazu SPD-6A UV Detector. A sample was eluted by 0.25 mol/L aqueous ammonium dihydrogen phosphate solution adjusted to pH 2.0 by an aqueous phosphoric acid solution and flowing at a rate of 1.0 mL/min in a Mightysil RP-18 column (4.6 mm i.d. × 150 mm in length) from Kanto Chemical Co, Ltd. Lactate was detected at 210 nm and the data were integrated by the Hitachi D-2000 Chromato-Integrator.

EXTRACTION MODEL

In the present system, TOMAC (Q^+Cl^-) extracts lactate (L^-) by forming the complex of tri-*n*-octylmethylammonium (TOMA, Q^+) and lactate with an ion exchange reaction at the interface between the aqueous and organic phases (Eq. 1). In stripping, the reverse reaction occurs.

$$L^- + Q^+Cl^- \overset{K^*}{\rightleftarrows} Cl^- + Q^+L^- \tag{1}$$

K^*, the extraction equilibrium constant, is defined with equilibrium concentrations of each component, $C_{mn}{}^*$, as follows:

$$K^* \equiv \frac{(C^*{}_{wCl}\, C^*{}_{oQL})}{(C^*{}_{wL}\, C^*{}_{oQCl})} \tag{2}$$

Although an hydroxyl ion is involved in the ion exchange reaction at high pH, it was not considered in the present analysis because the experiment was performed at pH < 6.0.

A kinetic analysis was carried out based on the 2-film theory shown in Fig. 1. The symbols, C_{wL}, C_{oQCl}, C_{wCl}, and C_{oQL} represent the concentrations of lactate in the aqueous phase, TOMAC in the organic phase, chloride in the aqueous phase, and the TOMA-lactate complex in the organic phase, respectively. Mass balance equations in batch operation are expressed as follows according to Eq. (1) because the volumes of aqueous and organic phases were identical:

$$C_{oQCl} = C_{oQCl,\,0} - C_{oQL} = C_{oQCl,\,0} - (C_{wL,\,0} - C_{wL}) \tag{3}$$

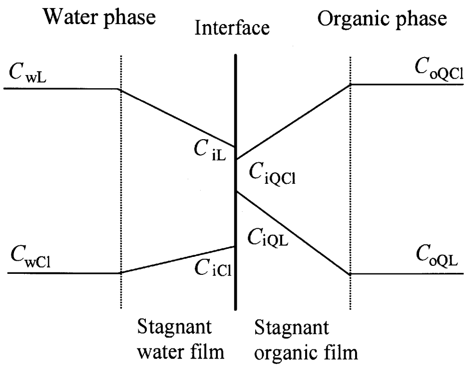

Figure 1. Two-film model.

$$C_{wCl} = C_{wCl,0} + (C_{wL,0} - C_{wL}) \tag{4}$$

$$C_{oQL} = C_{wL,0} - C_{wL} \tag{5}$$

where the subscript 0 represents the initial concentration.

The rates of lactate disappearance in the aqueous phase and TOMAC in the organic phase, and rates of chloride appearance in the aqueous phase and the TOMA-lactate complex in the organic phase are given as follows:

$$-\frac{dC_{wL}}{dt} = k_{wL}\,a(C_{wL} - C_{iL}) \tag{6}$$

$$-\frac{dC_{oQCl}}{dt} = k_{oQCl}a(C_{oQCl} - C_{iQCl}) \tag{7}$$

$$\frac{dC_{wCl}}{dt} = k_{wCl}a(C_{iCl} - C_{wCl}) \tag{8}$$

$$\frac{dC_{oQL}}{dt} = k_{oQL}\,a(C_{iQL} - C_{oQL}) \tag{9}$$

where *a* is the specific interfacial area, which is defined as interfacial area divided by the volume of each phase.

At quasi steady state, these rates are equal because of equimolar ion exchange, and then

$$k_{wL}a(C_{wL} - C_{iL}) = k_{oQCl}a(C_{oQCl} - C_{iQCl}) = k_{wCl}a(C_{iCl} - C_{wCl}) = k_{oQL}a(C_{iQL} - C_{oQL}) \tag{10}$$

The ratio of the mass transfer coefficients in the aqueous phase and that in the organic phase are replaced with β and γ to reduce the number of parameters to be determined.

$$\beta \equiv \frac{k_{\mathrm{WL}}}{k_{\mathrm{WCl}}} \tag{11}$$

$$\gamma \equiv \frac{k_{\mathrm{oQCl}}}{k_{\mathrm{oQL}}} \tag{12}$$

The extraction equilibrium prevails at the interface, and the constant K^* is expressed as follows:

$$K^* = \frac{C_{\mathrm{iCl}}\,C_{\mathrm{iQL}}}{(C_{\mathrm{iL}}\,C_{\mathrm{iQCl}})} \tag{13}$$

By combining Eqs. (10–13), the rate equation of lactate in the aqueous phase for both extraction and stripping is expressed as follows:

$$\frac{\mathrm{d}C_{\mathrm{wL}}}{\mathrm{d}t} = a\left[-\left(\frac{p}{2}\right) + \left(\frac{p^2}{4-q}\right)^{1/2}\right] \tag{14}$$

where

$$\begin{aligned} p = {} & (k_{\mathrm{wL}}C_{\mathrm{wL}} + k_{\mathrm{oQCl}}C_{\mathrm{oQCl}})\left(1-\frac{\mathrm{K}^*}{\beta\gamma}\right) + k_{\mathrm{wL}}C_{\mathrm{wCl}} \\ & \left(\frac{\gamma}{K^*}-\frac{1}{\beta}\right) + k_{\mathrm{oQCl}}C_{\mathrm{oQL}}\left(\frac{\beta}{K^*}-\frac{1}{\gamma}\right) \end{aligned} \tag{15}$$

$$q = k_{\mathrm{wL}}k_{\mathrm{oQCl}}\left[C_{\mathrm{wL}}C_{\mathrm{oQCl}}\left(1-\frac{\mathrm{K}^*}{\beta\gamma}\right) + C_{\mathrm{wCl}}C_{\mathrm{oQL}}\left(\frac{1}{\beta\gamma}-\frac{1}{K^*}\right)\right] \tag{16}$$

RESULTS

Time Courses of Lactate Concentration

The lactate concentration in the aqueous phase, C_{wL}, was determined by direct analysis of samples with HPLC, whereas the TOMA-lactate complex concentration in the organic phase, C_{oQL}, was calculated from a mass balance equation (Eq. 5). Figures 2a and 2b show the effect of initial lactate concentration in the aqueous phase on the time courses of lactate concentration during extraction. Because the plots overlapped at an early stage of extraction, as shown in Fig. 2b, the lactate concentration does not appear to affect the initial rate.

Figures 3a and 3b show the effect of initial TOMAC concentration in the organic phase. The initial extraction rate increased with increased extractant concentration.

Figures 4a and 4b show the effect of initial chloride concentration in the stripping phase on the time courses of lactate concentration during stripping. The effect of the chloride concentration on the initial stripping rate was not observed as shown by the plots, which completely overlap at an early stage.

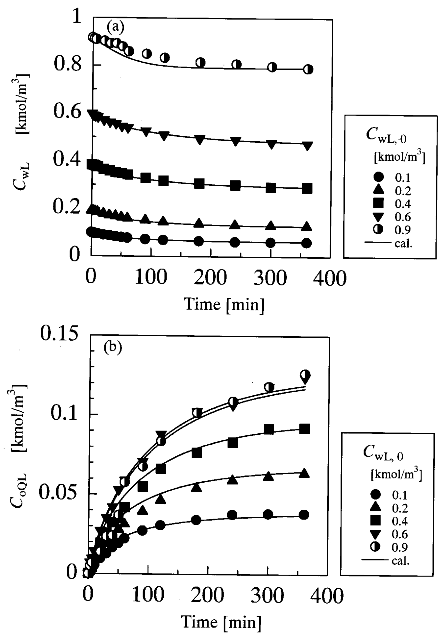

Figure 2. Effect of initial lactate concentration in the water phase on time courses of lactate concentration in (a) the water phase and (b) the organic phase at $C_{oQCl,\,0} = 0.5$ kmol/m^3.

Figures 5a and 5b show the effect of the initial TOMA-lactate complex concentration in the organic phase during stripping. The initial stripping rate increased with an increase in the complex concentration in the organic phase.

Analyses with 2-Film Theory

Equations (14–16) were used to roughly fit experimental results to a line by which the initial rates of extraction were calculated. The values of β and γ were determined based on Wilke and Chang's equation by replacing the molecular volume with 0.6 power of molecular weight.

$$\beta \equiv \frac{k_{WL}}{k_{wCl}} = 0.576 \tag{17}$$

$$\gamma \equiv \frac{k_{oQCl}}{k_{oQL}} = 1.08 \tag{18}$$

The values of k_{wL} and k_{oQCl} were obtained by the curve-fitting method to minimize the square sum of the difference between the experimental and calcu-

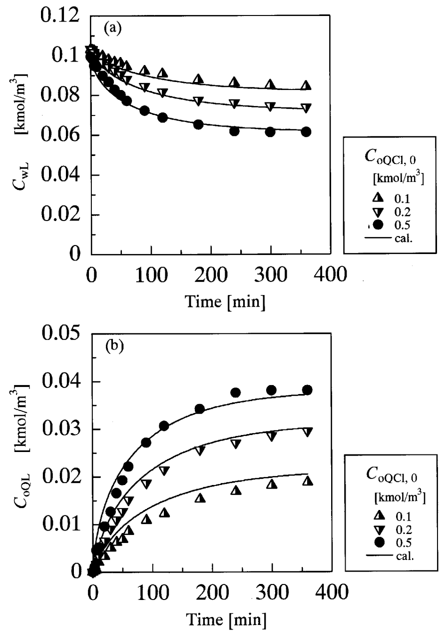

Figure 3. Effect of initial TOMAC concentration in the organic phase on time courses of lactate concentration in (a) the water phase and (b) the organic phase at $C_{wL,0} = 0.1$ kmol/m^3.

lated values, $\Sigma\Delta^2$. Using the results of rough fitting, the initial rates were obtained from Eq. (14) from which p and q were derived as follows:

for extraction: $C_{wCl} = C_{oQL} = 0$ at $t = 0$, and

$$p = (k_{wL}C_{wL} + k_{oQCl}C_{oqCl})\left(1 - \frac{K^*}{\beta\gamma}\right) \tag{19}$$

$$q = k_{wL}\, k_{oQCl}\, C_{wL}\, C_{oQCl}\left(1 - \mathrm{K}^*\, \beta\gamma\right) \tag{20}$$

for stripping: $C_{wL} = 0$ at $t = 0$, and

$$p = k_{wL}\, C_{wCl}\left(\frac{\gamma}{K^*} - \frac{1}{\beta}\right) + k_{oQCl}\, C_{oQCl} \\ \left(1 - \frac{K^*}{\beta\gamma}\right) + k_{wQCl}C_{oQL}\left(\frac{\beta}{K^*} - \frac{1}{\gamma}\right) \tag{21}$$

$$q = k_{wL}\, k_{oQCl}\, C_{wCl}\, C_{oQL}\left(\frac{1}{\beta\gamma} - \frac{1}{K^*}\right) \tag{22}$$

Figures 6a and 6b show the dependences of extraction rate on initial lactate concentration in the aqueous phase and the initial extractant concentration in the organic phase, respectively. The extraction rate was independent of initial lactate concentration, whereas it was directly proportional to the initial extractant concentration in the organic phase.

Figures 7a and 7b show the dependences of stripping rate on initial chloride concentration and initial TOMA-lactate complex concentration in the organic phase, respectively. The stripping rate was independent of initial chloride concentration, whereas it was directly proportional to the initial complex concentration. Based on these results, we determined that the diffusion through the organic film was the rate-controlling step. In fact, the estimated values of mass transfer coefficients in the aqueous phase were 2 or more orders higher than those in the organic phase, and $\Sigma\Delta^2$ was little affected by increasing mass transfer coefficients in the aqueous phase.

Analyses With the Simplified Model

Equations (14–16) were simplified based on the assumption that the diffusion through the organic film was the rate-controlling step. Because the concen-

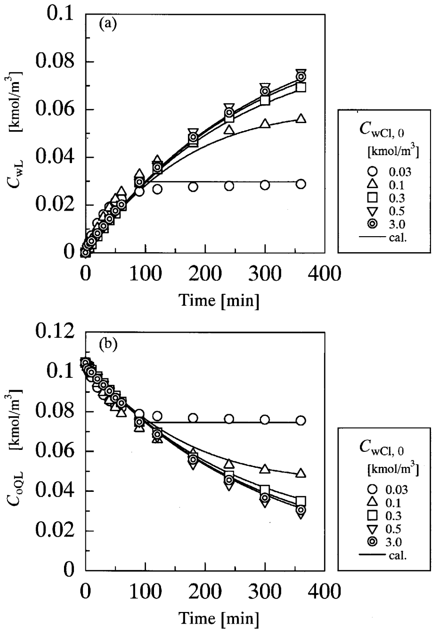

Figure 4. Effect of initial chloride concentration in the stripping phase on time courses of lactate concentration in (a) the stripping phase and (b) the organic phase at $C_{oQL,0} = 0.1$ kmol/m^3.

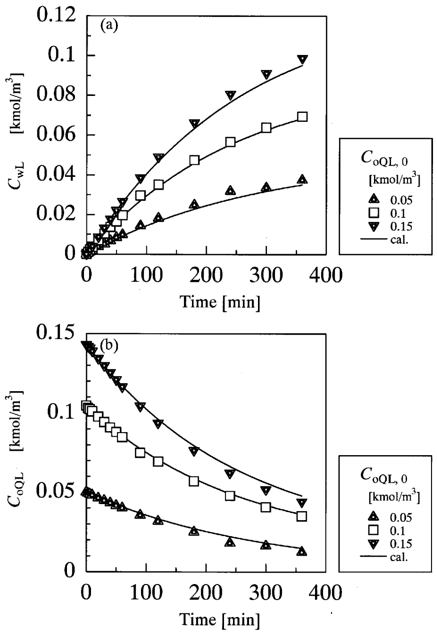

Figure 5. Effect of initial TOMA-lactate complex concentration in the organic phase on time courses of lactate concentration in (a) the water phase and (b) the organic phase at $C_{wCl,0} = 0.3$ kmol/m^3.

tration change in the aqueous film was negligible, Eq. (13) can be rewritten as follows:

$$K^* = \frac{(C_{wCl}\, C_{iQL})}{(C_{wL}\, C_{iQCl})} \tag{23}$$

When Eqs. (10–12) and Eq. (23) are combined, the rate equation of lactate in the aqueous phase is expressed as follows:

$$\frac{dCwL}{dt} = a\left[\frac{(-C_{wL}\, C_{oQCl}\, K^* + C_{wCl}\, C_{oQL})}{\dfrac{C_{wL}\, K^*}{k_{oQCl}} + \dfrac{k_{oQCl}\, C_{wCl}}{\gamma}}\right] \tag{24}$$

The value of k_{oQCl} was determined by the curve-fitting method to minimize the value of $\Sigma\Delta^2$. Three kinds of k_{oQCl} and k_{oQL} were derived by using the data of extraction runs, of stripping runs, and all the data of extraction and stripping runs. The results are shown in Table 1. The calculated time courses of lactate concentration shown in Figs. 2–5 were simulated with Eq. (24) with the coefficients of

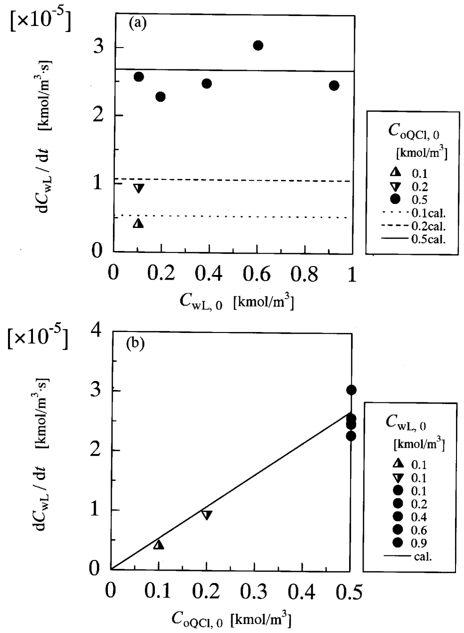

Figure 6. Dependences of extraction rate on (a) initial lactate concentration in the water phase and (b) initial TOMAC concentration in the organic phase.

combined extraction and stripping shown in Table 1c. The initial rates were also calculated with the following equations using the combined extraction/stripping coefficients shown in Table 1c.

for extractions: $C_{\mathrm{wCl}} = C_{\mathrm{oQL}} = 0$ at $t = 0$, and

$$\frac{\mathrm{d}C_{\mathrm{wL}}}{\mathrm{d}t} = ak_{\mathrm{oQCl}}\, C_{\mathrm{oQCl}} \tag{25}$$

Table 1. Values of Mass Transfer Coefficients Obtained with Three Different Sets of Experimental Data

Data Used	k_{oQCl} (m/s)	k_{oQL} (m/s)
a. Extraction	1.82×10^{-6}	1.69×10^{-6}
b. Stripping	2.25×10^{-6}	2.08×10^{-6}
c. Extraction and stripping	2.03×10^{-6}	1.88×10^{-6}

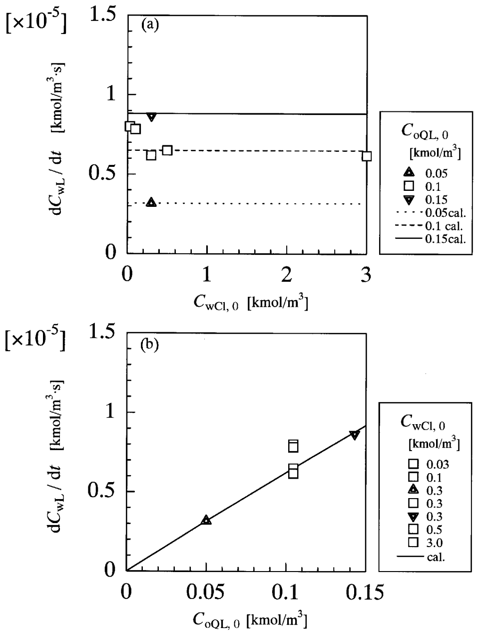

Figure 7. Dependences of stripping rate on (a) initial chloride concentration in the stripping phase and (b) the initial TOMA-lactate complex concentration in the organic phase.

for stripping: $C_{\mathrm{wL}} = 0$ and $t = 0$, and

$$\frac{\mathrm{d}C_{\mathrm{wL}}}{\mathrm{d}t} = \frac{ak_{\mathrm{oQCl}}\,C_{\mathrm{oQL}}}{\gamma} \tag{26}$$

The lines shown in Figs. 6 and 7 were calculated with above equations.

DISCUSSION

The dependence of extraction rates on the concentration of various species was first examined through the usual kinetic studies. However, in the present extraction system, the exact initial rates were difficult to obtain from the initial slope of lactate time courses because, as shown in Figs. 2–5, the rates decreased remarkably at an early stage of extraction and stripping. Though the straight time-course line can be obtained by decreasing the specific interfacial area, another problem inhibited the accuracy of the chemical analysis. These difficulties were caused by relatively low extractability of lactate and rapid extraction equilibrium in the TOMAC/oleyl alcohol extractant solvent. Hence, we attempted to determine unknown parameters by the curve-fitting method. This method has an advantage because all experimental points in the time course of lactate concentration can be used effectively.

The experimental results were first analyzed with the rate equations (Eqs. 14–16) based on the 2-film theory, but the mass transfer coefficients in aqueous-phase film could not be determined accurately. The initial rates were then calculated from the results of rough curve fittings, as shown in Figs. 6 and 7, and we speculated that the diffusion through the organic film was the rate-controlling step. Consequently, the rate equation of only the organic-phase film, Eq. (24), was applied to the present extraction system. Three kinds of k_{oQCl} and k_{oQL} were derived by using the data of extraction runs, the data of stripping runs, and all the data of extraction and stripping runs. Those results were shown in Table 1. Next, the dependence of the summation of residual squares, $\Sigma\Delta^2$, on the mass transfer coefficient in the aqueous phase, k_{wL}, was examined to estimate the order of k_{wL} values through the rate equations that are based on the 2-film theory. The results are shown in Fig. 8 in which three kinds of $\Sigma\Delta^2$ were calculated by using the corresponding sets of mass transfer coefficients shown in Table 1. Figure 8 shows that $\Sigma\Delta^2$ was fairly high at low k_{wL} and became constant at $k_{wL} > 8 \times 10^{-6}$ m/s in all cases. Furthermore, we observed an increase in extraction rates with increased stirring rates. Accordingly, we suggested that the diffusion through the organic-phase film was the rate-controlling step. High viscosities of TOMAC and oleyl alcohol, 100 times and 30 times higher than that of water, respectively, were considered the reason for the diffusion rate-controlling step.

The rate equations based on only the organic-phase film are very simple because of the 2 parameters of the organic phase, and these equations could satisfactorily explain the experimental results shown in Figs. 2–5. In theory, the kinetic

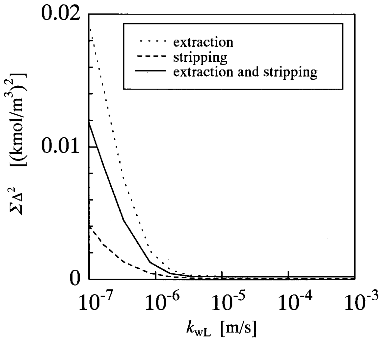

Figure 8. The relationship between k_{wL} and $\Sigma\Delta^2$.

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parameters determined with extraction-run data should agree with those from stripping-run data. However, value differences were observed in these parameters. Accordingly, the extent of agreement between experimental and calculated results is presented in Fig. 9 with three parameters that reflect all the data of extraction and stripping runs. A clear difference between data types was not observed. Consequently, the combined extraction/stripping parameters described in Table 1c were selected as the most appropriate source because all the data were used in the calculations.

The deviation between the experimental and calculated values was not negligible in the stripping operations of 0.03 kmol/m^3 sodium chloride concentration.

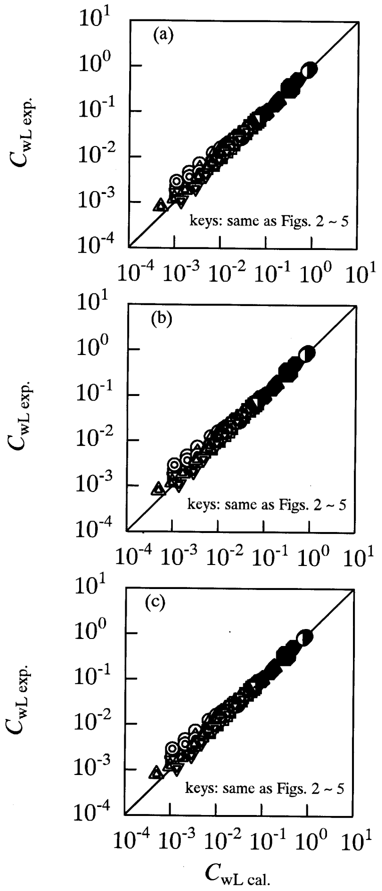

Figure 9. Comparison between experimental and calculated results with the kinetic parameters of Table 1a (a), Table 1b (b), and Table 1c (c).

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Under such low concentration, the experimental results could not be explained by the proposed model and we speculate that the kinetic parameters might have been altered. Though the measured lactate concentration gradually increased after 90 minutes, the calculation predicted the steady concentration of equilibrium state at approximately 100 minutes (Fig. 4). Although the stripping behavior in this case could not be explained, a problem may not exist: The stripping was not carried out under a low concentration of sodium chloride.

CONCLUSION

Extraction and stripping kinetics of lactic acid were investigated using tri-*n*-octylmethylammonium chloride as an extractant and oleyl alcohol as a diluent. Diffusion through the organic-phase film was determined as the rate-determining step because of the fairly high viscosity of the organic phase. The experimental results of both extraction and stripping could be explained satisfactorily by a simple equation that includes only 2 parameters.

NOMENCLATURE

a	specific interfacial area (m^2/m^3)
C_{mn}	concentration of component n in m phase or at the interface ($kmol/m^3$)
C^*	equilibrium concentration ($kmol/m^3$)
K^*	equilibrium constant ($-$)
k_{mn}	mass transfer coefficient of component n- in m-phase film (m/s)
t	time (s)
β	ratio of mass transfer coefficients in the aqueous phase ($-$)
γ	ratio of mass transfer coefficients in the organic phase ($-$)
$\Sigma\Delta^2$	square sum of the difference between experimental and calculated values ($(kmol/m^3)^2$)

Superscripts

*	equilibrium

Subscripts

initial	
Cl	chloride
i	interface

L	lactate
o	organic
QCl	TOMAC
QL	TOMA-lactate complex
w	aqueous

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